

XANES Spectroscopy of Ti and V Centers Grafted onto Mesoporous Sieves: Preliminary Results

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INTRODUCTION

Photochemical synthesis of a fuel by reduction of CO₂ using visible light as energy source and H₂O as electron source is one of the most attractive, yet unrealized goals in solar energy to fuel conversion. Photosynthesis of methanol for large scale use in fuel cells is considered a promising option for the replacement of fossil fuel combustion as a means of power generation. We are exploring photochemistry at the gas-solid interface of transition metal molecular sieves as a method for CO₂ conversion to methanol. A most critical aspect of this task is the reliable characterization of the framework of grafted metal centers in these materials, and the verification of the structural integrity of the photoreactor under use. X-ray absorption techniques, especially EXAFS (Extended X-Ray Absorption Fine Structure) and XANES (X-Ray Absorption Near Edge Structure) spectroscopy are the best tools for this type of solids. Based on earlier pre-edge X-ray absorption characterization of Ti silicalite materials at ALS beamline 9.3.1, we have recently been able to establish for the first time some of the key intermediates of carbon oxide reduction and H₂O₂ interaction in this molecular sieve.¹⁻³

In an effort to push the redox response of the metal centers from the UV towards visible photon energies, we are exploring the possibility of incorporating visible light-absorbing multinuclear assemblies into molecular sieves. A first step in the synthesis of such assemblies is the introduction of an anchor metal into the material in the form of a framework or grafted center. We have prepared grafted and framework Ti and V centers in mesoporous silicate sieves and have begun structural characterization of the materials by pre-edge absorption spectroscopy.

RESULTS

Using a specially designed sample holder for recording spectra of up to 12 molecular sieve samples in the form of pressed wafers in transmission or fluorescence mode, we have begun to record framework and grafted TiMCM41 and VMCM41 materials synthesized in our laboratory. As described by F. Schlachter in the ALS 2001 Compendium paper “ Beamline 9.3.1: Monochromator Upgrade”, the beam stability has been greatly improved since our earlier measurements. The new performance allows us to conduct reproducible scans over an energy range of several hundred eV, as demonstrated in Figure 1 by a 500 eV scan covering the Ti K-edge and the Ba L₃-edge of BaTiO₃. The spectrum shows the result of a single scan. The sample was a pressed wafer (diameter 1 cm, thickness 100 micron) of BaTiO₃ crystallites embedded in a silicate matrix. The measurement was conducted in transmission mode using a Si photodiode detector (Hamamatsu model S2744-08).

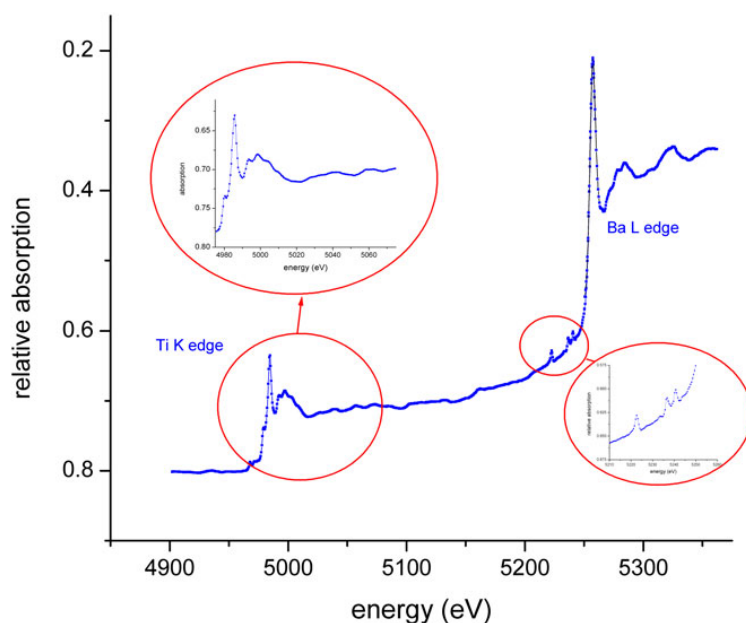


Figure 1. X-ray-absorption spectrum of crystalline barium titanate.

Figure 2a shows the absorption spectrum of framework TiMCM41 sieve in which 1 percent of the Si atoms are isomorphically substituted by Ti. Since the framework sites are tetrahedrally coordinated by oxygen, Ti in such sites gives rise to a sharp 1s-3d transition (A_1-T_2 component) absorbing around 4970 eV. By contrast, any extraframework TiO_2 clusters would feature octahedrally coordinated Ti that only contributes to the K-edge absorption but not to the pre-edge peak (optically forbidden). Figure 2a shows that the intensity of the 1s-3d peak relative to the height of the plateau between K-edge and the onset of the extended region is greater than 0.7. This is indicative of 100 percent framework substitution of the Ti, with no extraframework Ti oxide clusters present in the pores.

Similarly, the pre-edge peak of the grafted TiMCM41 spectrum shown in trace b of Figure 2 indicates that at least 90 percent of the Ti is in tetrahedral coordination. Diffuse reflectance UV and transmission FT-IR spectra of the material imply that the tetrahedrally coordinated Ti centers are tripodal (Si-O)TiOH moieties, i.e., the Ti is covalently anchored to three Si centers on the surface of the pore. Next, measurements will be conducted on recently prepared grafted VMCM materials.

These preliminary measurements establish the high degree of covalent anchoring of Ti as isolated centers in our mesoporous silicate materials. The quality of the single scan results displayed in Figure 1 and 2 shows that the recent monochromator upgrade at beamline 9.3.1 opens up routine XANES and EXAFS measurements up to energies of 5500 eV.

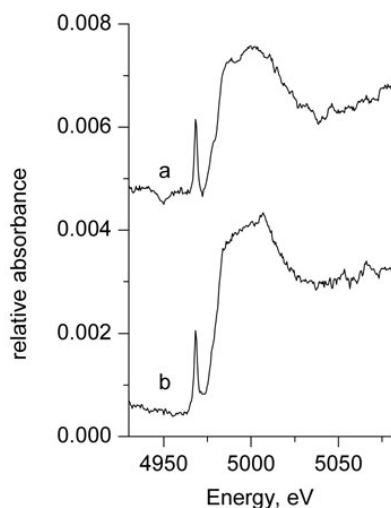


Figure 2. XANES spectrum of framework-substituted Ti-MCM41 (a), and grafted Ti-MCM41 (b).

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